

EXCHANGE INTERACTIONS IN SYMMETRICAL TRIADS OF PARAMAGNETIC IONS

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The inadequacy of the Heisenberg–Dirac–Van Vleck simple model (HDVV)¹ $J(S_i S_j)$ for description of the collective interactions of magnetic centres in solids is well known. Therefore, the reason for interest in the analysis of possible non-Heisenberg terms in the Hamiltonians of exchange interactions in different specific situations and in the possibility of their experimental study is quite clear.

We should stress that up to now the experimental determination of the order of asymmetrical interaction has met with considerable difficulties. These difficulties occur because in studying exchange-coupled pairs the asymmetric exchange operator matrix elements within one multiplet are zero. From this point of view the case when three similar exchange-coupled ions are situated at the vertices of an equilateral triangle is exceptionally favourable.

In fact, the largest in order of magnitude, the isotropic exchange interaction, leaves the triad energy levels with equal values of the total spin S degenerate. For example, for the triad $d^3-d^3-d^3$ we have two multiplets with $S = 1/2$, four with $S = 3/2$ etc. Therefore the effects caused by anisotropic interaction are manifested even in the first order of perturbation theory, and consequently, are simpler for experimental study.

The possible forms of the anisotropic interaction, which is quadratic in spin variables for all point-groups of a symmetrical triad, are found by means of group theory². The magnetic dipole–dipole Hamiltonian taking into account the g factor anisotropy of every ion completely contains all the operator forms thus found.

The consideration of an equilateral triangle of paramagnetic ions has led to the following results.

(i) The fine structure of the ground state $S = 1/2$ of the symmetrical antiferromagnetic triad ($J < 0$) is due to the Z component of the Dzyaloshinsky-Moriya asymmetric interaction^{3,4}.